MANUFACTURE OF CARBON/CARBON COMPOSITES BY HOT PRESSING

[0001] This application is a Non-Provisional Utility application which claims benefit of co-pending U.S. Patent Application Serial No. 60/430,497 filed December 3, 2003, entitled "Manufacture of carbon/carbon composites by hot pressing" which is hereby incorporated by reference.

[0002] We, Dai Huang, a citizen of China, residing at 232 Seiberling Drive, Sagmore Hills, OH; Richard T. Lewis, a citizen of the United States, residing at 595 Mock Orange Circle, Auburn, OH; Irwin C. Lewis, a citizen of the United States, residing at 17100 Valley Creek, Strongsville, OH; have invented a new and useful "Manufacture of Carbon/Carbon Composites by Hot Pressing."

BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

[0004] The present application relates to a method for forming carbon/carbon composites having a friction additive suited for use as friction-bearing and structural materials for high temperature applications. It finds particular application in conjunction with a composite material formed by resistance heating of carbon fiber/binder mixtures during application of a compressive force and will be described with particular reference thereto. It should be appreciated that the method has application in other areas where the combined effects of pressure and temperature are desired.

DISCUSSION OF THE ART

[0005] Carbon/carbon composites include those structures formed from a fiber reinforcement, which itself consists primarily of carbon, and a carbon matrix derived from a thermoplastic binder, such as pitch, or a thermosetting resin, such as a phenolic resin. Such materials are useful in applications where high temperature frictional properties and high strength to weight ratio are important. For example, carbon/carbon composites are known to be effective for providing thermal barriers and friction-bearing components, particularly in aircraft, aerospace vehicles, and high performance road vehicles. Carbon/carbon composites have been used for forming brake pads, rotors, clutches, and structural components for these vehicles. They tend to exhibit good temperature stability (often up to about 3000 °C, or higher), high temperature friction properties (typical coefficients of friction are in the range of 0.4-0.5 above

500-600 °C), high resistance to thermal shock, due in part to their low thermal expansion behavior, and lightness of weight. Thermal insulation materials formed from certain types of carbon fibers exhibit excellent resistance to heat flow, even at high temperatures.

[0006] A common method of forming carbon/carbon composites begins with lay-up of a woven fiber fabric or pressing a mixture of carbonized fibers derived from pitch (e.g., mesophase pitch or isotropic pitch), cotton, polyacrylonitrile, or rayon fibers, and a fusible binder, such as a phenolic resin or furan resin. In the process, the fibers are first impregnated with resin to form what is commonly known as a prepreg. Multiple layers of the prepreg are assembled in a mold of a heated press. The prepreg is compressed while simultaneously applying heat to the mold at temperatures of 200 °C-350 °C for a period of six hours or more to cure the resin fully. The fiber and cured resin composite is then heated at a slow rate to a final temperature of about 800°C in a separate operation to convert the binder to carbon. This carbonization step is carried out in an inert atmosphere and often takes about eighty hours to complete. Typically, the density of the carbon composite thus formed is up to about 0.6 to 1.3 g/cm^3.

[0007] For applications such as brake components and other friction-bearing applications, a density of about 1.7 g/cm^3 or higher is generally desired. To reduce voids in the pressure and heat-treated preform and increase its density, the preform is infiltrated with a phenolic resin or other carbonizable matrix material using a vacuum followed by pressure and the infiltrated material is then carbonized by heating. Densification is also often accomplished by chemical vapor infiltration (CVI) or chemical vapor deposition (CVD). The selected infiltration process is generally repeated six to ten times before the desired density is achieved. A final processing step

may include graphitization of the preform by heating it in an inert atmosphere to a final temperature not exceeding about 3200 °C. Above this temperature, carbon from the composite material tends to vaporize.

[0008] The lengthy heating and infiltration times render such composites expensive and impractical for many applications. For example, it may take about five months to form a carbon/carbon composite article, depending on the number of densification steps. Accordingly, sintered metal articles are commonly used for thermal applications, despite their greater weight and often poorer thermal stability and friction properties.

[0009] The present invention provides a new and improved method of forming a dense carbon/carbon composite, which overcomes the above-referenced problems and others.

SUMMARY OF THE INVENTION

[00010] In accordance with one aspect of the present invention, a method of forming a composite material is provided. The method includes combining carbon-containing fibers, a carbonizable matrix material, and a friction additive to form a mixture and heating the mixture to a sufficient temperature to melt at least a portion of the matrix material. The heating step includes applying an electric current to the mixture such that heat is generated within the mixture. While heating the mixture, a pressure of at least 35 Kg/cm^2 is applied to the mixture to form a compressed composite material.

[00011] Aspects of the invention include a second embodiment of adding the friction additive to the carbon/carbon ("C/C") composite. This aspect of the invention includes

combining carbon-containing fibers and a carbonizable matrix material to form a mixture and heating the mixture to a sufficient temperature to melt at least a portion of the matrix material. The heating step includes applying an electric current to the mixture such that heat is generated within the mixture. While heating the mixture, a pressure of at least 35 Kg/cm^2 is applied to the mixture to form a compressed composite material. The friction additive is incorporated into the compressed composite material by impregnation.

[00012] In accordance with another aspect of the present invention, an apparatus for forming a compressed composite material is provided. The apparatus includes a vessel, which defines a cavity for receiving a material to be treated. A means for applying pressure applies a pressure of at least 35 kg/cm^2 to the material in the cavity (e.g., a dual action ram or a single action ram). A source of electrical current applies a current through the material to resistively heat the material. A temperature detector detects the temperature of the material. A control system controls the pressure applying means and the source of electrical current such that the mixture is sequentially heated at a first temperature and pressed at a first pressure for a first period of time, and heated at a second temperature higher than the first temperature and pressed at a second pressure higher than the first pressure for a second period of time.

[00013] In accordance with another aspect of the present invention, a method of forming a composite material suitable for vehicle brakes is provided. The method includes compressing a mixture of carbon fibers, a matrix material that includes pitch, and an optional friction additive. During the step of compressing, a current is applied to the mixture. The mixture provides sufficient electrical resistance to the current such that the mixture reaches a temperature of at

least 500 °C to form a compressed preform. A carbonizable material is impregnated into voids in the compressed preform to form an impregnated preform. The product may be heated to carbonize the carbonizable material. The impregnation and baking steps are optionally repeated. The impregnated preform is graphitized to a final temperature of at least about 1500 °C to form the composite material. Preferably, the composite material has a density of at least 1.7 g/cc within two impregnation steps.

[00014] In accordance with another aspect of the present invention, a method of forming a composite material suitable for vehicle brakes is provided. The method includes compressing a mixture of carbon fibers and a matrix material which includes pitch. During the step of compressing, a current is applied to the mixture. The mixture provides sufficient electrical resistance to the current such that the mixture reaches a temperature of at least 500 °C to form a compressed preform. A friction additive is impregnated into the compressed preform. A carbonizable material may also be impregnated into voids in the compressed preform. The product may be heated to carbonize the carbonizable material. The carbonizable material impregnation and baking steps are optionally repeated. The impregnated preform is graphitized to a final temperature of at least about 1500 °C to form the composite material. Preferably, the composite material has a density of at least 1.7 g/cc within two impregnation steps.

[00015] An advantage of at least one embodiment of the present invention is that carbon-carbon composites, such as insulation materials or brake component materials, are formed in much shorter periods of time than by conventional hot pressing methods.

[00016] Another advantage of at least one embodiment of the present invention is that the density of the hot pressed material is higher than in conventional preforms, thereby enabling desired densities to be achieved with fewer densification and carbonization cycles.

[00017] Another advantage of at least one embodiment of the present invention is that a composite material is formed using fewer processing steps.

[00018] An additional advantage of the invention is that the carbon/carbon composite which includes the friction additive has an higher coefficient of friction than the carbon/carbon composite without the additive. A further advantage is that the invention may be used to incorporate the additive substantially uniformly through out the carbon/carbon composite.

[00019] A further advantage of the inventive carbon/carbon composite which includes the friction additive is that inventive composite has improved oxidation stability as compared to a carbon/carbon composite without such friction additive.

[00020] Still further advantages of the present invention will be readily apparent to those skilled in the art, upon a reading of the following disclosure and a review of the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[00021] FIGURE 1 is a side sectional view of a hot press according to the present invention.

[00022] FIGURE 2 is a flow chart showing steps of an exemplary process scheme for forming a carbon/carbon composite material having the additive according to the present invention.

[00023] FIGURE 3 is a chart of the fade test characteristics of composites made in accordance with the invention, a composite without the friction additive, and a commercially available product.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

[00024] A method of forming a carbonaceous material suitable for use in thermal applications, such as friction components, employs resistance heating of a mixture of a carbon reinforcement material, such as carbon fibers, and a matrix material, such as powdered pitch. Optionally, the mixture may also include an additive (the additive may also be referred to as a "filler") or the additive may be added to the carbonaceous material after forming the mixture. The resistance heating step is accompanied by application of mechanical pressure to densify the mixture. After hot-pressing, the compressed composite or "preform" is preferably subjected to one or more infiltration steps employing a carbonizable resin or binder to increase the density of the composite material. The densified preform is then heat-treated to a final temperature of up to about 3200 °C to remove remaining non-carbon components, such as hydrogen and heteroatoms (*e.g.*, nitrogen, sulfur, and oxygen), and form a carbon/carbon composite material, which is almost exclusively carbon.

[00025] An exemplary hot press **10** suited to resistively heating and compressing the mixture is shown in FIGURE 1. The hot press includes a mold box **12**, which defines a

rectangular cavity **14**, shaped to receive the mixture **16** of fibers, optional additive and matrix material. The cavity is surrounded on four sides **18** by a block or panels **20** of an insulation material, such as a refractory material, which is both electrically and thermally insulative. Pressure is applied to the mixture by upper and lower pistons **22, 24**, which are pushed toward each other by application of a compressive force to one or both of the pistons. It will be appreciated that the compressive force may alternatively or additionally be applied from opposed sides **18** of the mixture. Alternatively, pressure may only be applied by one of pistons 22 or 24. In the case that pressure is applied by only one piston, the press may be referred to as a single-action ram. The press illustrated in Figure 1 may be referred to as a dual action ram for at least the reason that pressure is applied from two pistons 22, 24.

[00026] A hydraulic system **30**, or other suitable system for applying pressure to the piston(s) **22, 24** urges the pistons together. A resistive heating system **32** applies a current to the mixture. The resistive heating system includes first and second electrodes, which are in electrical contact with the mixture. In a preferred embodiment, the pistons **22, 24** also serve as electrically conductive members, *i.e.*, as the first and second electrodes, respectively, and are formed from an electrically conductive material, such as steel. In an alternative embodiment, the electrodes are separate elements, which may apply the current from the same direction as the pistons **22, 24**, or from a different direction (*e.g.*, through the sides **18** of the hot press).

[00027] The resistive heating system **32** includes a source of electrical power for providing a high current at low voltage, such as an AC supply **40**. High DC currents are also contemplated. The AC or DC supply is electrically connected with the electrodes **22, 24** by

suitable electrical wiring **42, 44**. The mixture of optional additive, matrix material, and fibers **16** is sufficiently conductive to allow current to flow through the mixture and complete an electrical circuit with the first electrode **22** and second electrode **24** and power source **40**, while having sufficient electrical resistance to generate heat within the mixture **16** as the current flows between the electrodes **22, 24**. The heating rate is preferably at least 100 °C/min and can be as high as about 1000 °C/min, or higher. The resistance heating rapidly heats the entire mixture **16** to a suitable temperature for removal of volatile materials and carbonization of the matrix, typically in a matter of a few seconds or minutes, creating voids or bubbles within the mixture. Mechanical pressure is applied to densify the mixture **16** as the applied heat drives off the volatile materials.

[00028] The hot press **10** is preferably contained within a chamber **50** of a thermally insulative housing **52**. An exhaust system (not shown) optionally removes volatile gases from the chamber **50**.

[00029] The construction of the hot press **10** is such that all parts of the mixture **16** within the cavity **14** are subjected to a uniform pressure and to a uniform current flow. This results in the product having substantially uniform characteristics throughout the mass and which is substantially free of fissures and other irregularities, which tend to result in fracture during use.

[00030] A control system **60** monitors the current applied to the mixture **16** and other parameters of the system. For example, the temperature of the mixture **16** is measured with a thermocouple **62**, or other temperature monitoring device, mounted through the block **20** of the hot press or in a passage in thermal contact therewith. Displacement of the pistons **22, 24**

relative to each other is detected with a displacement detector **64** from which estimates of the mixture density can be made. The control system **60** receives signals from the thermocouple **62** and displacement detector **64**, corresponding to the temperature and linear displacement, respectively, and measurements of electrical current, voltage across the material from the current source **40**, and hydraulic pressure from the hydraulic system **30**. A processor **66** associated with the controller **60** compares the detected measurements with a preprogrammed set of desired values and instructs the control system to adjust certain parameters, such as the applied current, voltage, and/or hydraulic pressure, to achieve a product with the desired characteristics in terms of density, composition, and so forth.

[00031] With reference to FIGURE 2, a flow chart representing the sequence of steps involved in an exemplary embodiment of the manufacture of a carbon/carbon composite material is shown.

[00032] In Step 1, a carbon reinforcement material, preferably including carbon fibers, is combined with a matrix material and optionally a friction additive. The matrix material acts as a binder and a filler to fill gaps between the fibers. Preferably, the mixture **16** includes about 20-80% by weight of fibers and about 20-50% of the matrix material, more preferably, less than about 40% of the matrix material, and optionally about 0-30% of the friction additive, more preferably about 3-25% of the friction additive, even more preferably 5-20% of the friction additive, by weight. Other carbonizable and carbonaceous additives may be incorporated into the mixture. For example, a carbon material, which is electrically more conductive than the fibers or matrix material, such as powdered graphitized carbon, may be added to the mixture to

increase the conductivity of the mixture if the resistance is too high for current to flow during resistive heating.

[00033] Suitable carbon fibers for use as the reinforcement material include those formed from pitch, such as mesophase pitch or isotropic pitch, polyacrylonitrile (PAN), rayon, cotton, cellulose, other carbonizable materials, and combinations thereof.

[00034] The particular choice of carbon fibers depends on the anticipated end use of the composite material. For example, mesophase pitch carbon fibers provide the material with good thermal conductivity, once graphitized. Composites formed from mesophase pitch carbon fibers thus provide effective heat sinks for electronic components. Isotropic pitch carbon fibers exhibit a low thermal conductivity and provide good thermal insulation. PAN-based carbon fibers exhibit high strength and are thus suited to formation of structural components.

[00035] The fibers may be comminuted by a process such as chopping and/or milling. The carbon fibers preferably have an aspect ratio equal to or greater than 20:1, more preferably, greater than 100:1, a length of from about 2-30 mm, and a diameter of about 5-15 microns. Carbon reinforcements may also take the form of continuous filament yarn, chopped yarn, or tape made from continuous filaments and which are referred to as unidirectional arrays of fibers. Yarns may be woven in desired shapes by braiding or by multidirectional weaving. The yarn, cloth and/or tape may be wrapped or wound around a mandrel to form a variety of shapes and reinforcement orientations. For ease of handling, bundles of chopped filaments of about 0.2 cm to about 3 cm in length are preferred. Each bundle may comprise about 200-20,000 fiber filaments, each filament having a diameter of about 5-15 microns. Optionally, the bundles could

be of different lengths, with some bundles having relatively longer fibers (*e.g.,* 2-3 cm in length), while other bundles have relatively shorter fibers (*e.g.,* 0.2-1.0 cm in length). As used herein, the term "fibers" is intended to encompass all elongated carbon-containing reinforcement materials having a length which is at least twenty times, more preferably, at least 100 times the fiber diameter.

[00036] Exemplary fibers include mesophase pitch carbon fiber, obtained from Mitsubishi Chemical Corp., 520 Madison Ave., New York, or Cytec Industries Inc., 5 Garrett Mountain Plaza, West Patterson, NJ 07424, and PAN carbon fibers from Zoltek, Companies, Inc., 3101 McKelvey Rd, St Louis, MO 63044, or Toray Industries (America), Inc., 600 Third Ave., New York NY 10016.

[00037] The matrix material provides an independent source of carbon upon pyrolytic decomposition. The matrix material is fusible (*i.e.*, capable of melting) and contains both volatile and non-volatile components. The matrix material decomposes on heating to form an infusible material which is primarily carbon with the release of volatiles. Matrix materials which may be used to form carbon/carbon composites include liquids and solids which become sufficiently liquid or have low enough viscosity upon melting to coat the fibers. Preferred matrix materials are finely comminuted solids. However the invention is not limited to the use of finely comminuted solids, non-finely comminuted solids may also be used to practice the invention. Exemplary matrix materials include pitch, furan resins, and phenolic resins. Powdered pitch is a particularly preferred matrix material. Mesophase pitches and isotropic pitches with carbon yields of 60% or higher, more preferably, 70% or higher upon coking are particularly preferred

as matrix materials. These pitches are produced from petroleum or coal tar, although it is also contemplated that the pitch matrix material may be synthetically formed. Pitch/sulfur mixtures are also suitable as matrix materials. While the matrix material is described with particular reference to milled pitch powder, it will be appreciated that other matrix materials are also contemplated. However, for matrix materials with lower carbon content, such as phenolic resins, it has been found that the quantity of volatile components which are released during hot pressing is disadvantageous to forming a product of high density. It has also been found that pitch-based matrix materials yield a product with improved friction properties as compared with those employing phenolic resins.

[00038] The pitch or other matrix material is preferably in the form of a powder or other finely divided material having an average particle size of less than about 1000 microns, more preferably, less than 100 microns. The desired particle size can be achieved by milling or other comminution process. Exemplary pitch materials include coal tar pitches, available from Rutgers VFT AG, Reilly Industries, Inc., and Koppers Industries, Inc.

[00039] The matrix material and reinforcement material may be "dry mixed," *i.e.*, mixed without addition of solvents and at a temperature at which the matrix material is still a solid. More preferably, heat is applied during the mixing phase to raise the temperature of the matrix material above its softening point, which is about 70-350 °C in the case of pitch (Step 2). Preferably, the mixture is heated to about 30 °C or more above the Mettler softening point of the matrix material to reduce the viscosity of the matrix material. A Sigma-type mixer or similar is

preferably used to ensure the fibers and pitch are intimately blended. A blending time of about 10-30 minutes is generally sufficient.

[00040] While the process is preferably carried out in the absence of additional liquids, such as water or an organic solvent, it is also contemplated that a small amount of an organic solvent may be mixed with the matrix and reinforcement materials to act as a plasticizer for the matrix material and reduce the mixing temperature. Other methods, which involve forming a slurry with a volatile liquid and drying the slurry to form a preform, may also be used.

[00041] Preferably, the friction additive comprises elements or compounds that are carbides, oxides, or compounds that will react with available carbon atoms to form carbides and have sufficient temperature resistance to not decompose during any graphitization process, preferably stable at temperatures of about 2400 °C or higher. More preferably the additive comprises at least one of carbides, oxides, and combinations thereof. Examples of preferred carbides and oxides include compounds which include at least one of the following elements silicon, boron, titanium, molybdenum, vanadium, chromium, hafnium, zirconium, tungsten, and combinations thereof. Another suitable compound for a friction additive is an isotropic coke. Preferably the friction additive is in the form of a particle. Preferably, the particles have an average size of at least about 1 micron, more preferably 3 microns or more, up to about several hundred microns, less than about 1000 microns. Preferably, the size of the friction additive is measured in accordance with ASTM B 822, titled *Standard Test Method for Particle Size Distribution of Metal Powders and related Compounds by Light Scattering*. With respect to the additive, particle as used herein also includes a powder.

[00042] With continued reference to FIGURE 2, in Step 3, the mixture of carbon fibers, additive, and pitch powder is optionally packed into a separate mold from the mold box **12** of the hot press and pressed into a brick form having a density of about 0.5-1.0 g/cm^3 and dimensions only slightly smaller than those of the mold cavity.

[00043] In Step 4, the brick of fibers, additive, and pitch is transferred to the cavity **14** of the hot press mold box **12** (FIGURE 1). In an alternative embodiment, Step 3, and /or Step 2, is eliminated and the mixture of fibers, additive, and matrix material is transferred directly to the mold box **12** from the mixer. The lower piston/electrode **24** is raised to a position in which it forms a base of the mold cavity **14** prior to introduction of the mixture/brick **16**.

[00044] In Step 5, pressure is applied to compress the mixture **16**. The pressure applied is partly dependent on the desired final density of the composite material. In general, a pressure of at least about 35 kg/cm^2 is applied. The applied pressure can be up to about 150 kg/cm^2, or higher.

[00045] In Step 6, the mixture **16** is resistively heated while continuing to apply pressure to the mixture. It is also contemplated that heating may commence concurrently with, or before the start of application of pressure. Preferably, both heating and application of pressure are carried out concurrently, for at least a part of the process time, to densify the material as the volatile materials are given off.

[00046] The temperature of the mixture **16** during resistive heating is preferably sufficient to melt the pitch, remove at least some of the volatiles from the pitch, and facilitate compression

of the fiber matrix mixture as the pitch material is rigidized. It should be appreciated that, since pitch is generally not a homogeneous material, a portion of the pitch matrix material may remain unmelted (for example, quinoline insoluble solids tend not to melt), even at temperatures significantly above the softening point. Additionally, while substantially all the volatiles are removed in this step, it is also contemplated that a portion of the volatiles may remain without unduly affecting the properties of the material.

[00047] The mixture preferably reaches a temperature of above the carbonization temperature, which is about 500 °C in the case of pitch matrix material. For example, the mixture is heated to at least about 700 °C, more preferably, about 800-900 °C, although higher temperatures are also contemplated. The power input applied during resistive heating depends on the resistance of the mix and the desired temperature. For a mixture of pitch and carbon fibers, a power input of up to about 60kW/kg is applied, preferably in the range of 45-60kW/kg, for at least part of the heating process. For example, a power input of about 45-60kW/kg is applied for 90 seconds to 2 minutes, which may be preceded by application of pressure alone for about 3 to 5 minutes.

[00048] In another embodiment, a two-stage process is used. In a first stage (Step 6), a relatively low power input, preferably in the range of about 30kW/kg is applied for a period of about 30 seconds. In this stage, the temperature is preferably in the range of about 300 °C to 500 °C. The bulk of the volatiles are removed from the mixture in this temperature range. Above a certain temperature, about 500 °C in the case of pitch matrix material, the pitch becomes rigid (carbonizes) and it is more difficult to remove the volatiles from the mixture

without disruption of the structure. Accordingly, in the first stage, the temperature is preferably kept below the curing temperature of the matrix material.

[00049] In the second stage (Step 7), the temperature is increased to a higher temperature (*e.g.*, above about 700 °C, more preferably, 800-900 °C), sufficient to carbonize the matrix material. In this stage, the power input may be from about 45kW/kg to about 60kW/kg to bring the temperature up to about 800-900 °C. The power is maintained at this level for about 1-2 minutes, or longer. The optimum time depends on the applied power input, resistance, and other factors

[00050] The first and second stages are preferably also associated with different applied pressures. In the first stage (Step 6), for example, the pressure is lower than in the second stage (Step 7). The lower pressure reduces the opportunity for volatile gases to be trapped in the mixture, causing violent disruption of the mixture as they escape. For example, a pressure of about 35-70 kg/cm^2 is employed for the first stage, while an increased pressure of about 100-150 kg/cm^2 is employed for the second stage.

[00051] The resistance heating/pressing step (Step 6 and/or Step 7) takes under three hours, preferably, about 30 minutes or less, more preferably, less than about ten minutes, most preferably about 5-8 minutes, which is a much shorter time than the days required in conventional heating/pressing systems. Additionally, the density of the preform formed in this step is preferably at least 1.3 g/cm^3, more preferably, at least 1.4 g/cm^3, most preferably, about 1.5 to 1.7 g/cm^3. This is much higher than the density generally achieved in conventional methods, where the density of the fiber/matrix preform is about 0.6-1.3 g/cm^3 without further

densification procedures. As a consequence, fewer infiltration cycles (Step 9) are used to achieve a final desired density (generally 1.7-1.9 g/cm^3, more preferably 1.75-1.85 g/cm^3) with the resistive heating method than with conventional hot pressing methods. This decreases the number of processing steps and reduces the overall processing time even further. For example, where six or more infiltration steps are commonly used in a conventional process, the present process accomplishes a final density of about 1.75-1.85 g/cm^3 in only one or two infiltration steps. Whereas the conventional method may take several months from start to finished product, the present resistive heating method reduces the time to a matter of days or weeks.

[00052] In step 8, the hot-pressed preform is discharged from the mold cavity **14** and cooled. Preferably, the preform is cooled rapidly to a temperature below which oxidation does not occur at a significant rate. For example, the preform is immersed in water or sprayed with droplets or a mist of water to bring its temperature below about 400-500 °C. Alternatively, cooling may be achieved with an inert gas flow. Depending on the particular application of the carbon/carbon composite, it may be preferred that the preform is cooled at a rate to avoid cracking of the preform.

[00053] While the preform is readily formed in the shape of a rectangular brick, it is also contemplated that the mold cavity may be configured to produce a preform of a cylindrical or other shape, thereby reducing or eliminating the need for subsequent machining to form a desired component part.

[00054] Further densification of the cooled preform takes place in Step 9. In this step, a carbonizable material is impregnated into the preform body by pitch or resin impregnation. After

each impregnation step, the body is preferably rebaked in Step 9 to carbonize the carbonizable material. It has been found that a target density of about 1.6-1.8 g/cm^3 is readily achieved with only a single impregnation step. A density of 1.7 g/cm^3, or more, is readily achieved within two such Impregnation steps. In this process, the preform is placed in a vacuum chamber and the chamber evacuated. Molten pitch is introduced to the chamber and penetrates into the evacuated pores in the preform, with the aid of applied pressure.

[00055] In step 9, the body is heated slowly in a furnace, for example, at a heating rate of about 10 °C/hour to about 20°C/hour to a final temperature of about 800-900 °C. The body is preferably held at this temperature for about 2-3 hours and then the power is removed. The body is then cooled to a temperature of about 100 °C or less before being removed from the furnace. The body may be cooled slowly, such as over a period of two to three days depending on the size of the body. Alternatively, a cooling medium such as water may used to reduce the cooling time by spraying the medium on the body. Each carbonization step thus takes about 5-6 days to complete. Having fewer infiltration and carbonization cycles therefore reduces the overall densification time.

[00056] In an alternative densification process, the preform is exposed to an atmosphere of a gaseous hydrocarbon, such methane, ethane, propane, benzene, and the like, or a mixture thereof. The hydrocarbon gas decomposes, or is cracked, for example at a temperature of about 900°C to about 1,200°C to form elemental carbon, which is deposited within the carbon/carbon composite. This may be referred to as chemical vapor infiltration ("CVI").

[00057] In the case that the additive comprises an oxide, an embodiment of the invention may include a heat treating step, preferably after Step 9. Preferably the heat treating comprises heating the compressed composite material to a sufficient temperature for a sufficient period of time to convert at least a portion of the oxide additive to a carbide. For example, if the oxide comprises SiO_2, the heat treating step comprises heating the composite material to a temperature of at least about 1500 °C, such as at least about 1700 °C to about 1800 °C for a period of up to about 5 hours, such as about 2 to about 4 hours. Preferably, the heat treatment converts the SiO_2 into SiC. The invention does not require that the entire oxide additive is converted into a carbide, in practice one portion of the additive may remain in the oxide form and another portion of the additive may be converted to an oxide.

[00058] At Step 10, the body is subjected to a graphitization process. In this step, the body is heated in an inert atmosphere, for example, in an induction furnace, to a temperature of about 1500 °C, or higher, more preferably, about 2000 °C, most preferably, about 2400 °C-, to remove all (or substantially all) hydrogen and other heteroatoms and produce a carbon/carbon composite. In graphitizing the body, it is preferred that the body is not subjected to a temperature equal to or greater than the decomposition temperature of the friction additive, e.g., about 2600°C for SiC. Above about 2400 °C, the composite is fully graphitized. The carbonization temperature is selected according to the end use of the final product and is generally above the highest temperature to which the composite material is to be subjected in use.

[00059] During this carbonization or graphitization process, various physical properties of the composite material, such as its thermal and electrical conductivity, are substantially increased, making the composite material suitable for various high temperature commercial applications. The period of time for this procedure is calculated using conventional calculations based upon graphitization time/temperature kinetics, taking into account furnace thermal load and mass.

[00060] The invention further includes an alternative embodiment of incorporating the additive into the carbon/carbon material. As shown in FIGURE 2, the invention may include optional step 8A to incorporate the additive into the carbon/carbon composite. The friction additive may be impregnated into the compressed composite material. In the case of adding the friction additive by impregnation, suitable forms of the additive include at least colloidal suspensions and solutions.

[00061] Preferably the colloidal suspension comprises the additive in a concentration of at least about 20% up to about 75%, more preferably at least about 25% up to about 60% and even more preferably at least about 30 up to about 50%. Preferably the additive is in the form of about a micron or smaller particle, more preferably, a submicron sized particle. The additive may be suspended in any material which the additive is not soluble. It is also preferred that the material can readily may be vaporized, e.g., in the case that the additive comprises SiO_2, water comprises a suitable material to suspend the additive. The material may be referred to as a liquid carrier. An example of a preferred colloidal solution of the friction additive includes silicon dioxide 30% dispersion in water sold by Alfa-Aesar Co. of Ward Hill, MA.

[00062] In an embodiment, the friction additive is impregnated into the compressed composite material under vacuum. For example, the composite material may be placed in a vessel fitted with a vacuum outlet and the pressure inside the vessel is reduced below about 50 mm of mercury, preferably below about 10 mm of mercury. The friction additive contained in a separate vessel is then introduced through a connecting valve and the pressure inside the vessel including the composite is increased to atmospheric pressure or higher. Preferably, the composite material remains completely immersed in the liquid carrier of the friction material or the solution containing the friction additive for at least about 10 minutes at about atmospheric pressure or higher. The impregnated composite may then be removed from the vessel for further processing or Step 8A may optionally be repeated 1 or more times depending on the amount of additive desired in the composite. At the end of the friction additive impregnation step, any excess liquid in the vessel may be drained off. Also in the case that a vacuum pump is used to create the negative pressure (vacuum) in the vessel, it may be preferred that the vacuum pump is isolated from the vessel prior to introducing the friction additive.

[00063] Optionally, this embodiment of the invention may include the step of substantially removing the material which the additive is suspended in from the composite material. For example, if the material is water, the compressed composite, after impregnation, is dried to remove the water. After the material is substantially removed, the compressed composite containing the additive may be processed in the same manner as described above.

[00064] With respect to the timing of the impregnation of the composite body with the friction additive, the impregnation may take place before or after graphitization and it may also take place before or after the aforementioned carbon densification impregnation of the preform.

[00065] Though Step 8A has been introduced above as an alternative to including the friction additive in Step 1, if so desired, Step 1 with the friction additive may practiced along with optional Step 8A.

[00066] Once the general shape of the carbon/carbon composite article is fabricated, the piece can be readily machined to precise tolerances, on the order of about 0.1 mm or less. Further, because of the strength and machinability of carbon/carbon composites, in addition to the shaping possible in the initial fabrication process, carbon/carbon composites can be formed into a variety of shapes.

[00067] The resulting carbon/carbon composite material is suited to a wide range of applications, including use as brake components, antiskid components, and structural components, such as body panels, pistons, cylinders, for vehicles, such as aircraft, high performance cars, trains, and aerospace vehicles, missile components, and for use as susceptors in furnaces. The reduction in processing time achieved with the resistance heating method opens up many other applications for the material which have hitherto been impractical because of time and production cost constraints.

[00068] Typical properties of the carbon/carbon composites formed from mesophase pitch carbon fibers and milled pitch are as follows:

As-pressed density of the preform: 1.55-1.65 g/cm^3;

Final density after graphitization: 1.75-1.82 g/cm^3 (with two pitch impregnation/carbonization cycles)

Flexural strength: about 50 Mpa

Young's modulus: about 35 Gpa

Compressive strength: about 60 Mpa

Thermal conductivity: about 75 W/m•K.

[00069] The electrical conductivity of the graphitized material is generally in the range of about 9-10 μΩ-m. With the exception of thermal conductivity, these properties were measured perpendicular to the fiber orientation (perpendicular to the pressing direction). Thermal conductivity was measured in the fiber orientation direction.

[00070] Without intending to limit the scope of the invention, the following examples demonstrate the improvements in processing times which can be achieved with the resistance heating method.

EXAMPLES

EXAMPLE 1: Carbon/Carbon Composite Made by Dry Mixing of Precursor Materials

[00071] Mesophase pitch-based carbon fibers and a matrix material of milled pitch with 170 °C softening point ("SP") (ASTM D 3104) and 70% coking yield were dry mixed at ambient temperature in a Sigma-type blender or similar type of mixer for about 5-15 minutes. The ratio of fibers to pitch matrix material was from 50-80 wt % fiber: 20-50 wt % pitch. The mixture was

collected and charged into a mold box cavity (dimensions approximately 23 x 20 cm) of a hot press, as illustrated in FIGURE 1. A pressure of up to about 140 kg/cm^2 was applied to the mixture in the press. After pressing to compact the mixture, an electric current of about 1000-2000 amps (a power input of about 30-60kW/kg) was passed through the mixture. The mix was held under the temperature and pressure conditions for about 5-10 minutes. The temperature of the mixture reached 800-900 °C. This hot pressing process carbonizes and densifies the fiber/matrix mixture in a very short period of time, compared with conventional processes. The as-pressed material (preform) had a carbonized density of about 1.6 g/cm^3. The preform underwent two pitch impregnation cycles, each one followed by re-carbonization, to densify the material. Lastly, the preform underwent graphitization to a temperature of about 3200 °C to obtain a product having a density of about 1.75 g/cm^3.

EXAMPLE 2: Carbon/Carbon Composite Made by Hot Mixing of Precursor Materials

[00072] Various batches of mesophase pitch-based carbon fibers and a matrix material of milled pitch from Example 1 were hot mixed at a temperature of about 200 °C in a Sigma-type blender or similar type of mixer for about 30-45 minutes. The ratio of fibers to pitch matrix material was varied from about 50-80 wt % fiber: 20-50 wt % pitch. During the hot mixing, the matrix material coated the fibers uniformly. The mixture was collected and charged into a mold box cavity of a hot press, and heated and pressed as described for Example 1. Alternatively, the mixture was compacted in a separate mold to a density of between about 0.5 and 1.0 g/cm^3 prior to hot pressing.

[00073] A pressure of up to 140 kg/cm^2 was applied to the mixture in the hot press. After pressing to compact the mixture, an electric current as high as 1500-2000 A (a power input of about 45-60kW/kg) was passed through the mixture. The mix was held under the temperature and pressure conditions for about 5-10 minutes. The temperature of the mixture reached 800-900 °C. This hot pressing process carbonizes and densifies the fiber/matrix mixture in a very short period of time, compared with conventional processes. The as-pressed material (preform) had a carbonized density of between about 1.4 and 1.65 g/cm^3. The preform underwent two pitch impregnation cycles, each one followed by re-carbonization, to densify the material. Lastly, the preform underwent graphitization to a temperature of up to about 3200 °C to obtain a product having a density of about 1.70 to 1.75 g/cm^3.

[00074] TABLE 1 shows the as-pressed densities obtained for various fiber and pitch compositions (*i.e.*, prior to infiltration and graphitization).

TABLE 1

Carbon Fiber (wt %)	Pitch Binder (wt %)	As-pressed density (g/cc)
75	25	1.61
65	35	1.56
55	45	1.37
45	55	*

* The block cracked after hot-pressing.

[00075] As can be seen from TABLE 1, the as-pressed density decreased as the pitch binder concentration was increased. Thus for applications where high as-pressed density is desired, it is preferable to keep the pitch binder concentration below about 40-45%.

[00076] Samples of the as-pressed composites having an as-pressed density of about 1.55-1.65 g/cm^3 were subjected to two impregnation/carbonization cycles. In each impregnation step, petroleum pitch was impregnated into the composite. The samples to be impregnated were first heated to a temperature of about 250 °C for 6-8 hours and then placed in a pressure vessel, which had been preheated to at least 200 °C. A vacuum was pulled for 4-6 hours and then the vacuum pump was isolated and liquid pitch was introduced to the pressure vessel. Nitrogen was introduced to a pressure of 100 psig and the samples impregnated with the liquid pitch for 10-12 hours. The pressure was then released from the vessel and the impregnated composite samples retrieved after the excess liquid pitch was removed.

[00077] The impregnated composite was then carbonized by heating it in a furnace to a temperature of about 800-900 °C, using a heating rate of 10 °C/hour. The temperature was held for about 2-3 hours. The power was removed and the composite allowed to cool from about 900 °C toabout100 °C over a period of two to three days. The impregnation and carbonization steps were then repeated. The carbonized composite was then graphitized in an induction furnace by heating the material to a temperature of 3000 °C at a heating rate of 300 °C/hour. The final temperature of 3000 °C was maintained for approximately one hour. Tests on the graphitized composite material produced the following results:

Final density after graphitization: 1.75-1.82 g/cm^3

Flexural strength: about 50 Mpa

Young's modulus: about 35 Gpa

Compressive strength: about 60 Mpa

Thermal conductivity: about 75 W/m•K.

Electrical conductivity: about 9-10 μΩ-m.

EXAMPLE 3: Silicon Carbide Carbon/Carbon Composite Made by Hot Mixing of Precursor Materials

Direct addition of solid SiC.

[00078] Blends of silicon carbide powder with an average particle size of about 10-20 microns from Alfa Aesar Company were blended with mixtures of chopped mesophase pitch carbon fiber and a 170 °C SP coal tar pitch by stirring at about 220 °C. The mesophase pitch carbon fibers were about ¼-inch long obtained from Mitsubishi Chemical Corp. The following blend compositions were prepared, as shown in TABLE 3-1:

TABLE 3-1

	1	2	3	4
Carbon fiber	77%	69%	69%	62.5%
Matrix	19.2%	27.6%	17.2%	25%
SiC	3.8%	3.4%	13.8%	12.5%

[00079] The blends were hot pressed to produce carbonized 3 cm thick carbonized composites with dimensions of 23 cm x 23 cm. The densities measured for the as-pressed

composites were: (1) =1.52, (2) =1.53, (3) =1.55, and (4) =1.55 g/cc. The composites were impregnated with petroleum pitch and then rebaked to 900 °C; the impregnation and rebake steps were repeated. After the 2 impregnation/rebake cycles, the composites were graphitized by heating to about 2500 °C. Final densities for the composites were: 1.72 g/cc for (1) and (2) and 1.75 g/cc for (3) and (4). The final composites contained about 4 and 16% of silicon carbide respectively distributed uniformly throughout the composite.

Friction Testing of the SiC/C/C Composite

[00080] Composites were produced as in Example 3 using a blend of 10 parts of SiC powder to 25 parts of the 170°C SP (ASTM D 3104) pitch to 65 parts of chopped mesophase pitch carbon fibers. One composite artifact was subjected to 1 petroleum pitch impregnation ("1 PI") followed by rebake and graphitization while a second composite was subjected to 2 pitch impregnation/rebake cycles ("2PI") followed by graphitization. The final density for the 1 PI composite was 1.67 g/cc and 1.73 g/cc for the 2 PI material. Both composites were subjected to friction testing using the Chase Test. The Chase Dry Friction Machine is described in the web site of Greening Company of Detroit, Michigan where the test was carried out. As shown in Figure 3, the test results for the Silicon Carbide Carbon/Carbon Composites ("SiC/C/C") of 2 PI is compared to a Carbon/Carbon ("C/C") composite produced by the same process but without the addition of silicon carbide. Without the SiC the coefficient of friction is low at low temperatures, ~0.1 at about 100 °C, or less, and remains lower than the composite with the friction additive throughout the test, although the friction performance of the composite without the friction additive does improve with increasing temperature. For the SiC/C/C composites, the coefficient of friction remains high at about 0.3 at low temperatures and rises to above 0.4 at

high temperatures. The friction behavior is close to that shown for a commercial carbon/metallic brake material used in racing cars.

EXAMPLE 4: Silicon Carbide Carbon/Carbon Composite Made by Hot Mixing of Precursor Materials

Addition of silicon dioxide followed by thermal conversion to SiC

[00081] A hot-pressed composite was produced by adding about 10 parts of SiO_2 powder (~2 microns from Alfa Aesar Co.) to 25 parts of the pitch binder and 65 parts of fibers. The composite was then impregnated once with petroleum pitch and rebaked to ~ 900°C. The density after rebake was 1.65 g/cc. The impregnated composite was then heat treated up to ~1750°C and held at that temperature for about 5 hours to effect conversion of the SiO_2 to SiC by reaction with the carbon in the composite. The composite was then taken to ~2500°C and held at that temperature to effect graphitization. The final density of the composite was 1.46 g/cc. The reduced density is due to the loss of carbon from conversion of the SiO_2 to SiC. Microscopy examination of the composite showed that essentially all the SiO_2 had converted to SiC leaving ~ 7% SiC in the composite.

EXAMPLE 5: Silicon Carbide Carbon/Carbon Composite Made by Impregnation

Impregnation with colloidal SiO_2 followed by thermal conversion to SiC

[00082] Carbon/carbon composites were produced using 33% coal tar pitch binder and 67% mesophase pitch carbon fibers were impregnated with a colloidal suspension of SiO_2 particles in water. The as-pressed composites which contained no other additives had a density of ~1.54 g/cc after the 900 °C heat treatment in the pressing step. The SiO_2 was obtained from Alfa Aesar Co as a 30% aqueous suspension of 0.01 micron particles. The impregnations were carried out at 25 °C by subjecting the composites to a vacuum of about 0.4 mm. The pump was isolated and isolation was followed by introduction of the SiO_2 dispersion in water and then equalization of the pressure to 760 mm. The composites were then dried in a vacuum oven by heating slowly to remove the water. The final pressure in the oven was about 0.1 mm and the final temperature was about 175°C. The weight pickup of SiO_2 was measured as ~4.5%.

[00083] One of the composite samples was subjected to a second impregnation with the SiO2 dispersion and after water removal the total SiO_2 pickup was measured as ~7.5%. Both composite materials were then heated to 1750 °C and held there for 5 hours to effect conversion to SiC. The composites were then heated to 2500 °C for 1 hour to effect graphitization. The final composite densities were measure as 1.50 g/cc for the singly impregnated composite and about 1.47 g/cc for the twice impregnated composite. Examination by microscopy confirmed the conversion of the SiO_2 to SiC had occurred.

[00084] The invention has been described with reference to the preferred embodiment. Obviously, modifications and alterations will occur to others upon reading and understanding the preceding detailed description. It is intended that the invention be construed as including all

such modifications and alterations insofar as they come within the scope of the appended claims or the equivalents thereof.